

Trimethylsilylation of ordered and disordered titanasilicates: improvements in epoxidation with aqueous H₂O₂ from micro- to meso-pores and beyond†

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A novel method for trimethylsilylation of micro- and mesoporous titanasilicates using BSTFA [N,O-bis(trimethylsilyl)trifluoroacetamide] renders Ti-MCM-41 and SiO₂/TiO₂ aerogels active for olefin epoxidation with aqueous H₂O₂, and even improves the activity of TS-1.

The importance of hydrophobicity for titanasilicate catalyzed oxidation reactions with aqueous H₂O₂ has been the subject of much recent research. The hydrophobicity of the interior pores of titanasilicalite (TS-1) and Al-free Ti-beta renders them active for aqueous H₂O₂ oxidation of alkanes and alkenes.^{1,2} By comparison, Al containing Ti-beta is less efficient, mainly because of framework Al induced hydrophilicity.³ Because of their mesoporous nature (25–100 Å pores) Ti-MCM types^{4,5} would be useful as oxidation catalysts for larger, higher value molecules. However, Corma and coworkers⁵ observed that because of its hydrophilic nature, Ti-MCM-41 was much less effective for oxidation with aqueous H₂O₂ than even Al-Ti-beta. Therefore it is not surprising that efforts to render Ti-MCM's hydrophobic and hence, more active, were undertaken: Tatsumi *et al.*⁶ trimethylsilylated Ti-MCM-41 and Ti-MCM-48 using trimethylsilyl chloride and hexamethyldisiloxane and observed increased oxidation activity.⁴ Amorphous silica/titanias with even wider pores present opportunity for further increasing the range of oxidation substrates. Recently non-catalytic and hydrophilic amorphous silica/titanias have been made hydrophobic and catalytic by substituting alkoxy groups in the silica precursors with alkyl or phenyl groups during the sol-gel synthesis.^{7,8}

Herein we report a simple and effective technique for trimethylsilylation of microporous crystalline TS-1, mesoporous Ti-MCM-41(Ti-MCM), and SiO₂/TiO₂ aerogels (Ti-Agel). The resultant materials are hydrophobic and have enhanced activity for olefin epoxidation with aqueous H₂O₂.

TS-1 was synthesized by the method of Thangaraj and Sivasanker.⁹ Corma's method⁵ for the preparation of Ti-MCM-41 was modified by using a single precursor for titanium and silicon: Gelest diethoxysiloxane-ethyltitanate copolymer (no.

in Gelest catalogue = PSITI-019), [(EtO)₂SiO][(EtO)₂TiO], Si:Ti ≈ 15. The general method for the preparation of aerogel catalysts was that of Dutoit *et al.*,¹⁰ with acetylacetone-modified titanium isopropoxide. The sol-gel was continuously extracted with supercritical CO₂ at 40 °C at 24.2 MPa for 5 h. The resulting fluffy yellow powder was calcined at 400 °C for 1 h in N₂ followed by 600 °C for 5 h in air.

A typical procedure for the trimethylsilylation of catalysts is as follows: a mixture of N,O-bis(trimethylsilyl)trifluoroacetamide [CF₃COSiMe₃]₃=NSiMe₃ or BSTFA (1.0 g) and toluene (8 g) was added to the catalyst (0.5 g). The mixture was stirred for 2 h at room temperature, filtered, and the solids washed with toluene and air dried. The dried materials' hydrophobicity was evidenced by their floating on water. In addition, using a TGA method derived from Anderson and Klinowski¹⁷ we obtained the following hydrophobicities (mg water adsorbed silylated/mg water adsorbed non-silylated at 50 °C) for TS-1, Ti-MCM, and Ti-Agel respectively: 1.04, 0.41, 0.68. As expected, the ratio for trimethylsilylated TS-1 was near unity because trimethylsilylation is not expected to affect the interior pore system. However, for the mesoporous materials the ratio is less than unity consistent with trimethylsilylation of the accessible surface. Other trimethylsilylating agents such as trimethylsilyl chloride and hexamethyldisilazane were also used successfully. However, these required more severe conditions and, in the case of the chloride, resulted in loss of Ti from the aerogels. While BSTFA has been used to derivatize organics and end group cap chromatographic columns,¹¹ there is no reference to using it to modify catalysts. Characterization data for the catalysts are given in Table 1.

BSTFA treatment of TS-1 introduces IR bands consistent with trimethylsilylation. Because of the strong asymmetric stretch of the silicate lattice at *ca.* 1225–1230 cm⁻¹, we are unable to detect the diagnostic symmetric methyl deformation in the 1250–1260 cm⁻¹ region.¹² We do see the antisymmetric methyl deformation at *ca.* 1400 cm⁻¹, as well as bands at *ca.* 725 and 700 cm⁻¹ that may be assigned to the antisymmetric Si-C and the symmetric Si-C stretching modes, respectively.

Table 1 Characterization data for TS-1, Ti-MCM and Ti-Agel^a

$$\text{CF}_3\text{C}(\text{OSiMe}_3)=\text{NSiMe}_3 + 2 [\text{O}_3\text{Si}-\text{OH}]_s \rightarrow \text{CF}_3\text{CONH}_2 + 2 [\text{O}_3\text{Si}-\text{O}-\text{SiMe}_3]_s$$

Sample name	XRD ^b	IR/cm ⁻¹	I ₉₆₀ /I ₁₀₉₀	A ₁ , A ₂ (UV-VIS/nm)	A ₁ /A ₂ (UV-VIS/nm)	Si/Ti ICP	N ₂ adsorption		
							SA	PV	APD
TS-1	MFI	962	0.10	215, 258 ^d	1.34	26	485	0.11	52
TS-1-syl	MFI	972	0.05	207, 260	1.45	—	453	0.14	74
Ti-MCM	MCM-41	960	0.37	216, 268	0.97	8 ^e	810	0.12	27
Ti-MCM-syl	—	950	0.23	214, 269	0.99	—	727	0.14	24
Ti-Agel	Amorphous	959	0.34	214, 255	1.21	12	493	1.50	148
Ti-Agel-syl	—	955	0.32	214, 260	1.15	—	318	1.33	166

^a Elemental analysis by inductively coupled plasma spectroscopy (ICP): MCM: Ti-MCM-41, Ti-Agel: SiO₂/TiO₂ Aerogel, syl: trimethylsilylated I₉₆₀: assumed to be ν(Si-O-Ti);¹⁰ I₁₀₉₀: ν(Si-O-Si).¹⁰ A₁: absorbance of band due to isolated Ti. A₂: absorbance of band due to (Ti-O)_n oligomers. SA: BET N₂ surface area/m² g⁻¹. PV: BJH N₂ pore volume ml g⁻¹. APD: BJH N₂ av. pore diameter/Å. ^b No TiO₂ phases observed by XRD in any of the samples.

^c Position of 960 band, KBr pellet technique. ^d Si/Ti charged = 15. ^e Shoulder at ≈ 320 nm indicates anatase.

Bands near 1680 and 1750 cm^{-1} are assigned to the amide group of trifluoroacetamide (the silylation byproduct) and residual BSTFA, respectively. The IR spectrum of Ti-Agel is very similar to that of Ti-MCM, which is to be expected since the latter is composed of amorphous walls. For both Ti-MCM and Ti-Agel, silylation added bands to the IR spectra that can be attributed to SiMe_3 groups, especially the very distinctive band at 1250–1260 cm^{-1} , and the CH_3 rocking modes at *ca.* 840 and 755 cm^{-1} .¹²

The IR band at *ca.* 960 cm^{-1} (the 960 band) has been attributed to Si–O–Ti bonds as a fingerprint for tetrahedral Ti substitution in silicate lattices,¹⁰ or to Si–OH groups.^{13, 14} We hypothesize that for our TS-1 loss of silanol groups after trimethylsilylation results in a decrease in the 960 band intensity. The intensity of the 960 band of Ti-MCM decreased on silylation, in agreement with Tatsumi *et al.*⁶ However, the 960 band of Ti-Agel decreases only slightly upon trimethylsilylation, consistent with a smaller fraction of silanols available to the silylating agent compared to MCM. Based upon the pronounced hydrophobic nature of the silylated material these must be the ones which confer hydrophilicity to the base aerogel.

Analysis of the UV–VIS data¹⁵ for all of the base materials indicates the presence of isolated Ti and oligomeric $(\text{Ti-O})_n$ species; in addition, TS-1 and Ti-MCM are contaminated by anatase. The non-isolated Ti-species may have a detrimental effect on the epoxidation reaction, since they have been reported to decompose H_2O_2 homolytically.¹⁶ Ti-isolation, as measured roughly by the ratio of the absorbance of band due to isolated Ti to the band due to $(\text{Ti-O})_n$ oligomers, (A_1/A_2), is better for Ti-Agel compared with Ti-MCM. This may be ascribed to the acac modification performed on the Ti-precursor for Ti-Agel, which slows down the condensation rate of the hydrolyzed Ti species.¹⁰ The effect of trimethylsilylation on the UV–VIS spectra of the samples is not great, indicating that the silylation procedure probably did not result in reaction with the isolated Ti sites or H_2O_2 destroying sites.

N_2 adsorption measurements on Ti-MCM confirmed that surface area and pore size decrease on trimethylsilylation.⁶ Our Ti-MCM contains microporosity, probably related to the titania or silica/titania impurities resulting from the high Ti-concentration in the synthesis gel. For Ti-Agel, trimethylsilylation decreases surface area and mesopore volume as expected. Because of limitations in the N_2 adsorption techniques, the effect of trimethylsilylation on the microporosity of TS-1 could not be determined.

Trimethylsilylation of the available surfaces of TS-1, Ti-MCM, and Ti-Agel increased the efficiency of olefin epoxidation reactions with dilute aqueous hydrogen peroxide (Table 2). Especially striking were the results with Ti-MCM and the aerogels where epoxidation yields were dramatically increased after the treatment. Rendering the catalyst surfaces hydrophobic has either improved access of the olefin to the active sites or has diminished the inhibitory effect of water.¹ Either scenario should result in increased catalytic activity.

In the case of the TS-1 the improved activity after trimethylsilylation may be attributed to better wetting of the microcrystallite surface with the olefin. While it is possible that the increase in activity is related to loss of oligomeric $(\text{Ti-O})_n$ H_2O_2 decomposition sites after trimethylsilylation, lack of changes in the UV–VIS and the probably very low concentration of reaction sites for silylation argue against this.

It is important to note that the trimethylsilylation technique described in this communication results in nearly equivalent epoxidation activity for any of the titanasilicates studied, the only requirement being the presence of isolated, tetrahedral Ti sites. Especially striking is the treatment of normally inert aerogel; we believe this to be the first report of *post synthesis* activation of this material. In addition the expectation of

Table 2 Effect of trimethylsilylation on the epoxidation activity of Ti-Agel, Ti-MCM, and TS-1 titanasilicates^a

Catalyst	% H_2O_2	Olefin ^b	Epoxide yield ^c
Ti-Agel	10	1-Oct	0.2
Ti-Agel	10	COT	0.5
Ti-Agel-syl	10	1-Oct	6
Ti-Agel-syl	10	COT	32
Ti-MCM	3	1-Oct	0.5
Ti-MCM-syl	3	1-Oct	23.6
TS-1	10	1-Oct	2.4
TS-1	10	COT	0
TS-1-syl	10	1-Oct	12.9
TS-1-syl	10	COT	0.5

^a Reaction conditions: olefin (3 ml), aq. H_2O_2 (1 ml), catalyst (50–100 mg)^d stirred at room temperature for 24 h. ^b 1-Oct: oct-1-ene, COT: *cis*-cyclooctene. ^c Yield of the corresponding epoxide was based on initial H_2O_2 concentration. The only significant byproduct with oct-1-ene was octan-1-al (5–10%); with cyclooctene no byproducts were observed. ^d 100 mg with Ti-Agel and TS-1, 50 mg with Ti-MCM.

epoxidizing molecules too large to fit in the pores of TS-1 has been realized for the Ti-aerogel after the silylation treatment. *cis*-Cyclooctene is epoxidized readily by Ti-Agel-syl compared to almost no reaction with either TS-1 or TS-1-syl.

In summary we have demonstrated a general method for significantly increasing the activity of titanasilicate oxidation catalysts using aqueous hydrogen peroxide by rendering their surfaces hydrophobic by treatment with the trimethylsilylating agent BSTFA.

Notes and references

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